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Review of Anti-Reflection Sol-Gel Coatings in High Energy Lasers

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Review of Anti-Reflection Sol-Gel Coatings in High Energy Lasers
Madison, WI, United States
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Review of Anti-Reflection Sol-Gel Coatings in High Energy Lasers

GOMD 2016 Madison, WI
Symposium 5: Festschrift for Professor Donald R. Uhlmann
Session title: Legacy
Room: Madison
May 24, 2016 4:00PM

Tayyab Suratwala
Optics and Materials Science & Technology

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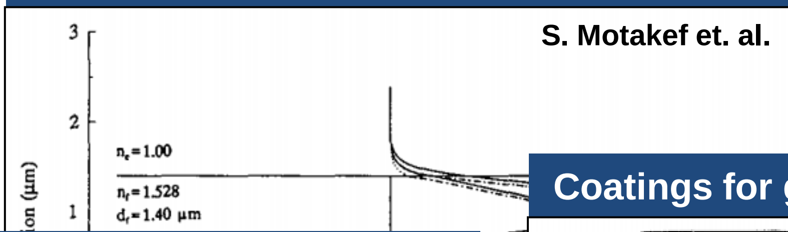
1963

Sol Gel derived materials is amongst the many scientific areas Prof. Uhlmann has contributed in his career

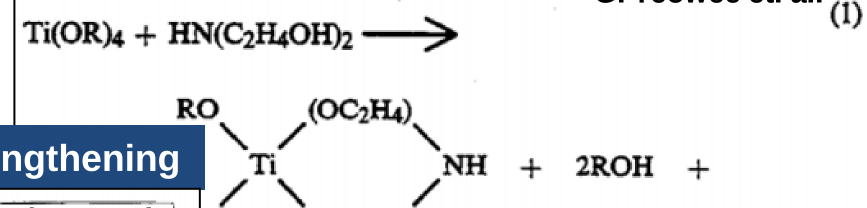
Optical Planar Waveguides

S. Motakef et. al.



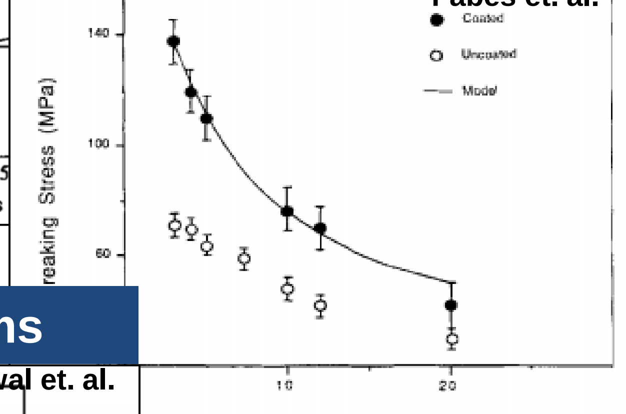
Ferroelectric PZT films

G. Teowee et. al.



Coatings for glass strengthening

Fabes et. al.

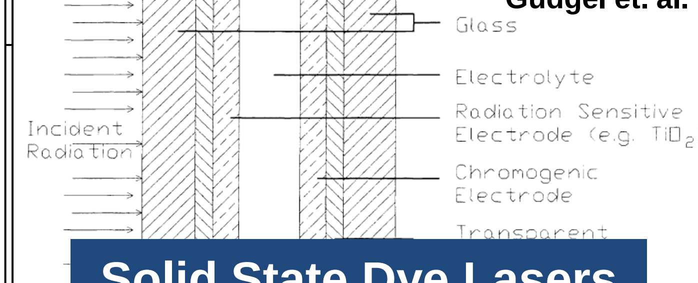


Crystallization

Zelinski et. al.

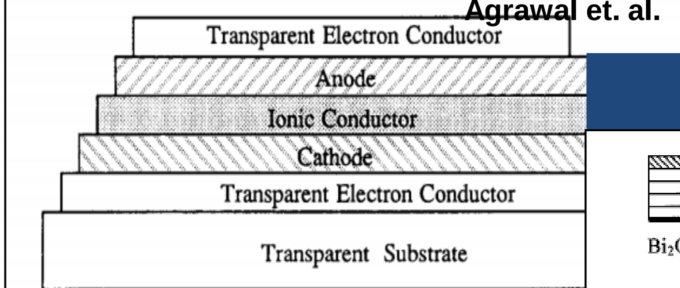
Photochromic Films

Gudgel et. al.



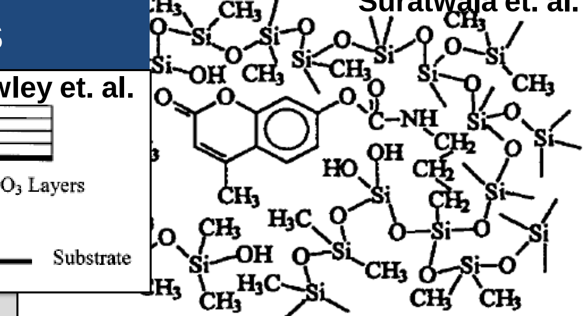
Electrochromic Films

Agrawal et. al.



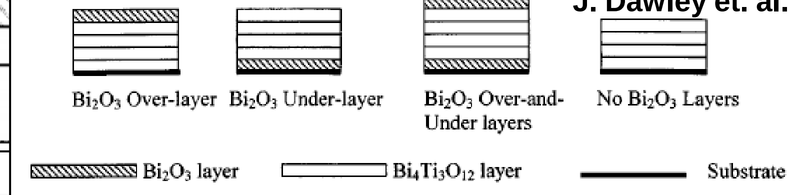
Solid State Dye Lasers

Suratwala et. al.



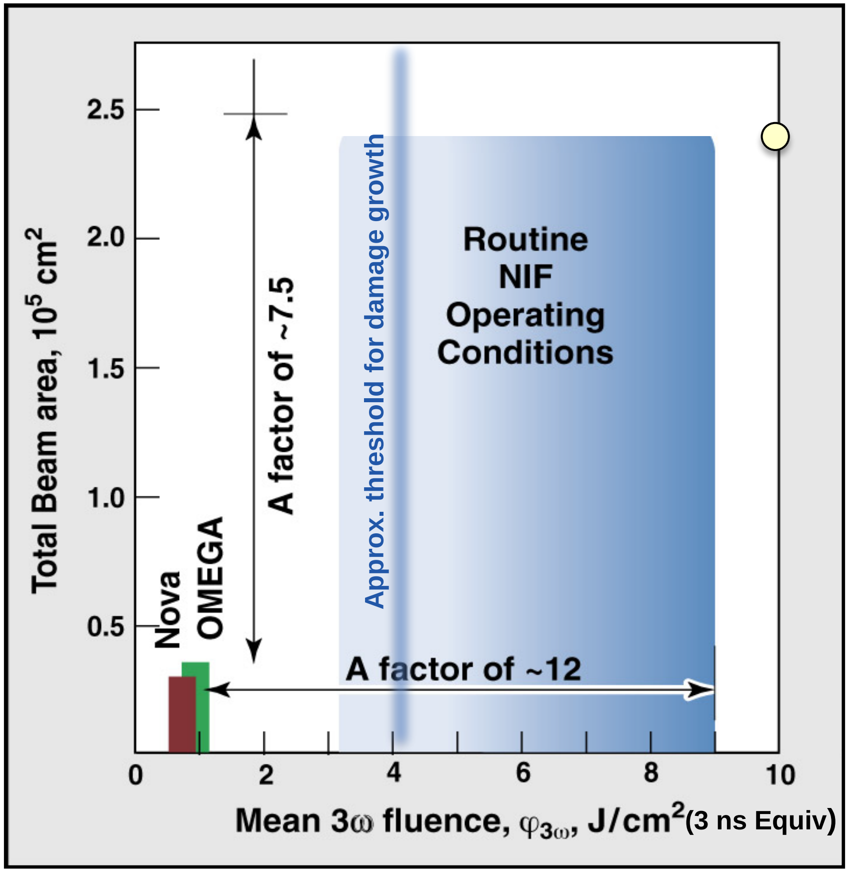
Bismuth titanate films

J. Dawley et. al.



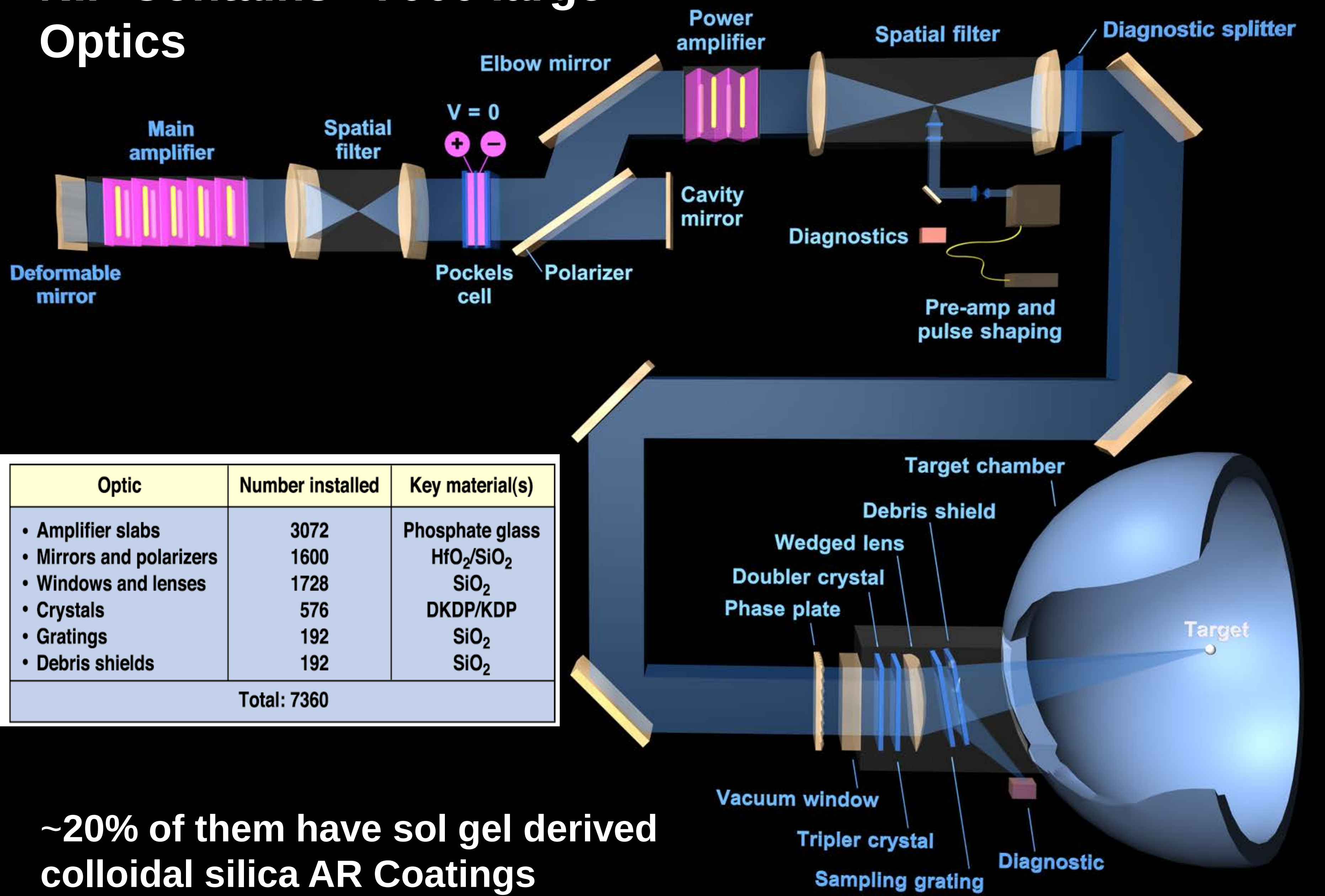
National Ignition Facility (NIF)

NIF is unique compared to all other lasers built to study Inertial Confinement Fusion



- The NIF 3ω energy specification of 1.8 MJ requires an order of magnitude increase in operating fluence over previous ICF lasers
- The optics loop recycle strategy allows NIF to operate above the 3ω damage limit

NIF Contains >7000 large Optics

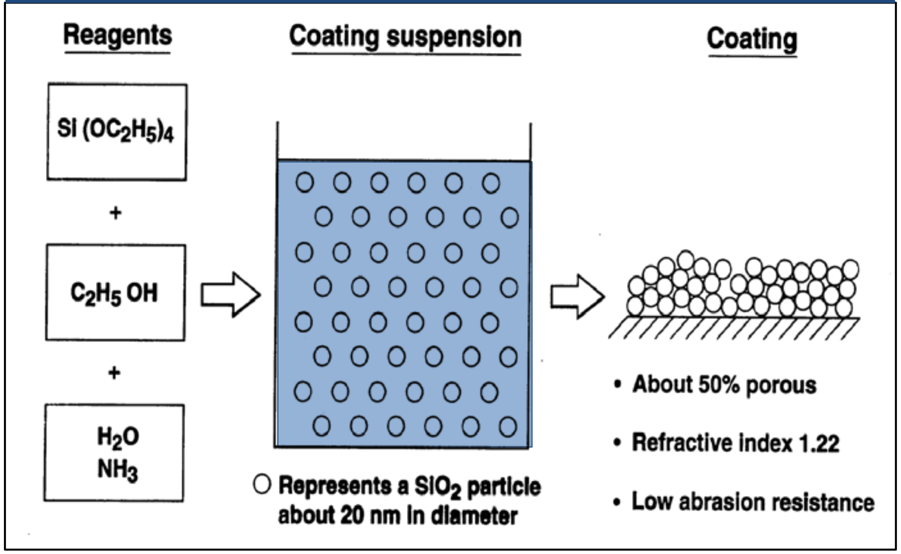


Optic	Number installed	Key material(s)
• Amplifier slabs	3072	Phosphate glass
• Mirrors and polarizers	1600	HfO_2/SiO_2
• Windows and lenses	1728	SiO_2
• Crystals	576	DKDP/KDP
• Gratings	192	SiO_2
• Debris shields	192	SiO_2
Total: 7360		

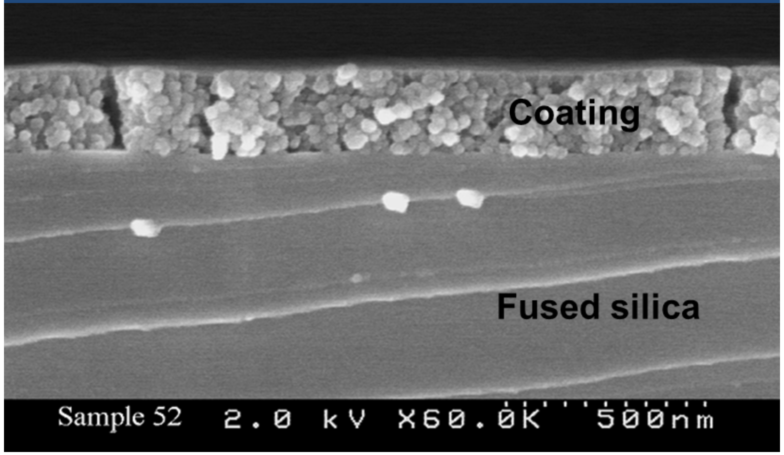
~20% of them have sol gel derived colloidal silica AR Coatings

Damage resistant antireflection (AR) coating are made from sol-gel derived colloidal silica

Stöber silica colloids are made by the sol-gel process



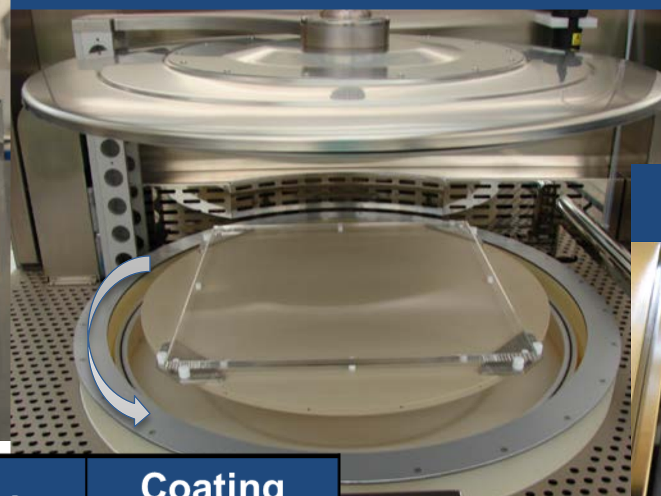
SEM cross section image of colloidal silica AR coating



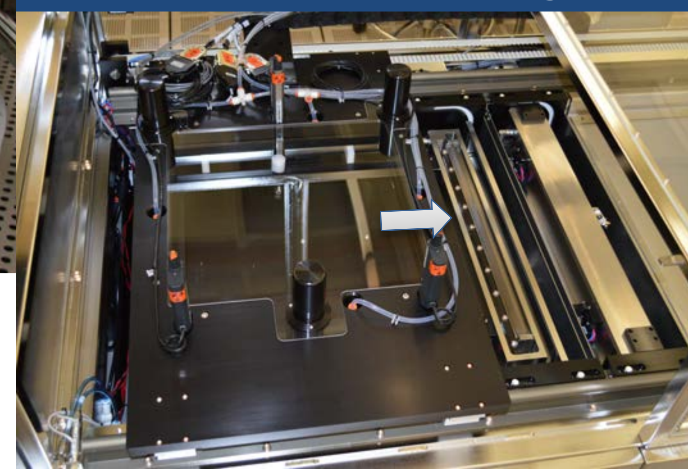
Three methods are used deposit the AR Coating on large optics using various sol compositions on various optics

Dip Coating

Spin Coating



Meniscus Coating



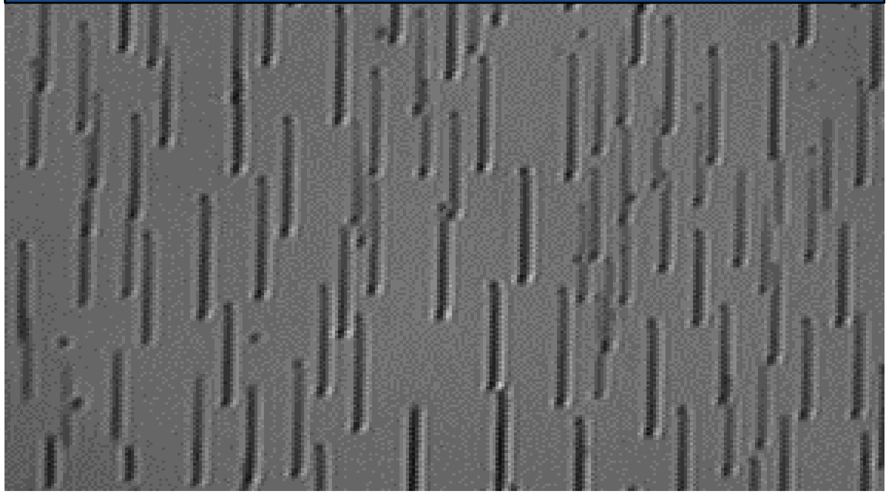
Material	Coating Solution	Coating Method
Borosilicate glass	Sol D in sec-butanol	Meniscus
Fused Silica	Sol A in ethanol	Dip coating (ammonia treated)
KDP KD*P	Sol D in sec-butanol Sol E in decane Sol D in ethanol	Spin Coating

Intermission Story

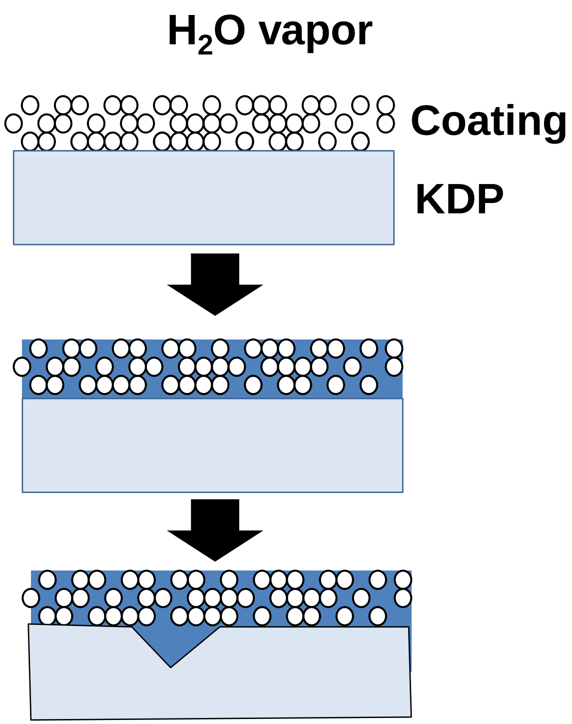
3+ hr Progress Meetings
+ Cigars

The silica colloid's hydrophilic nature is detrimental to KDP optics due to etchpit formation

Microscope images of etchpits KDP surface



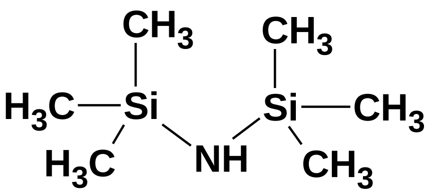
Formation of etchpits on KDP

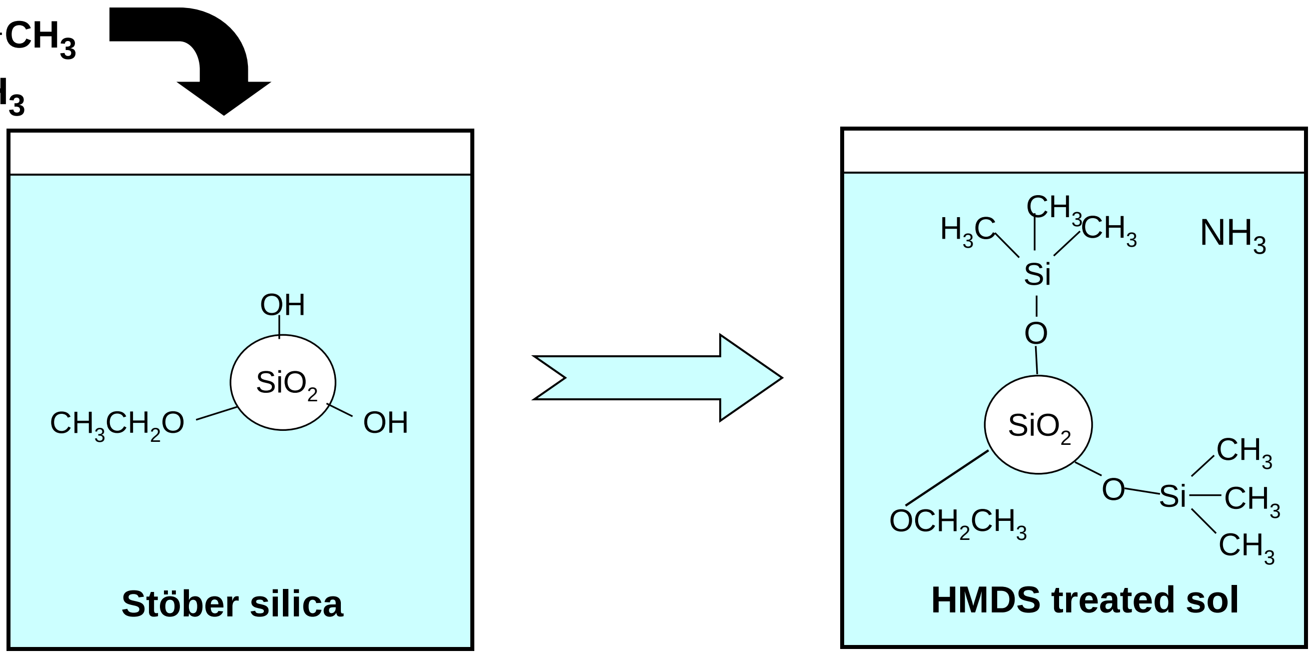


Hence, we developed a hydrophobic colloidal silica AR coating

Trimethylsilyl (TMS) sols are prepared by adding hexamethyldisilazane (HMDS)

Surface modification is performed in solution, not by vapor treatment



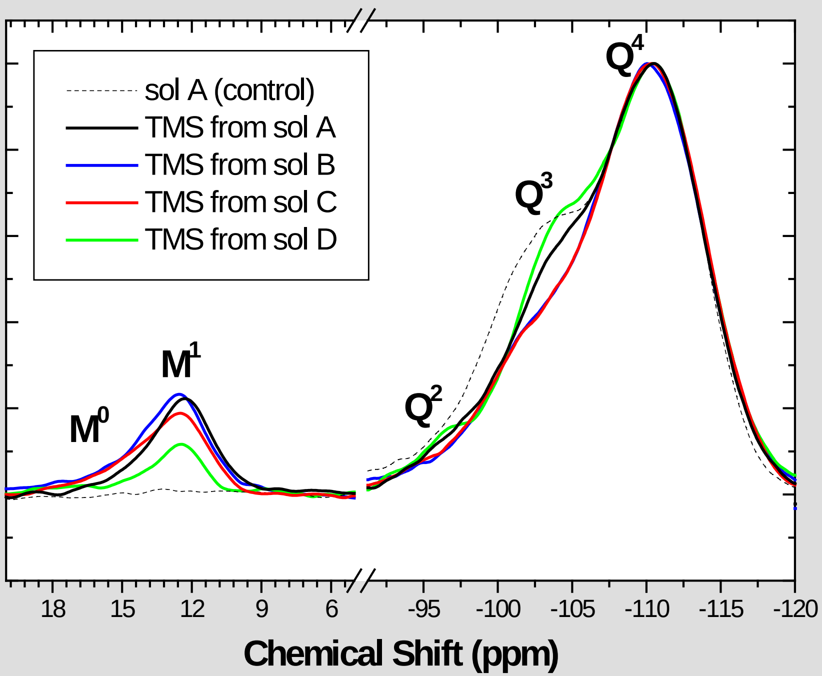


Degree of TMS functionalization, depends on:

1) Starting surface chemistry
2) Reaction time
3) Reactant concentration

Highest TMS coverage occurs using Sol B

TMS Sols: ^{29}Si MAS NMR Spectra



M^1 peak is due to TMS species

- **M^1 species replace Q^2 and Q^3 species which are surface silanol species**
- **Can quantify TMS coverage (C) as:**

$$C = \frac{A_{M_1} \cdot 100\%}{A_{M_1} + A_{Q_2} + A_{Q_3}}$$

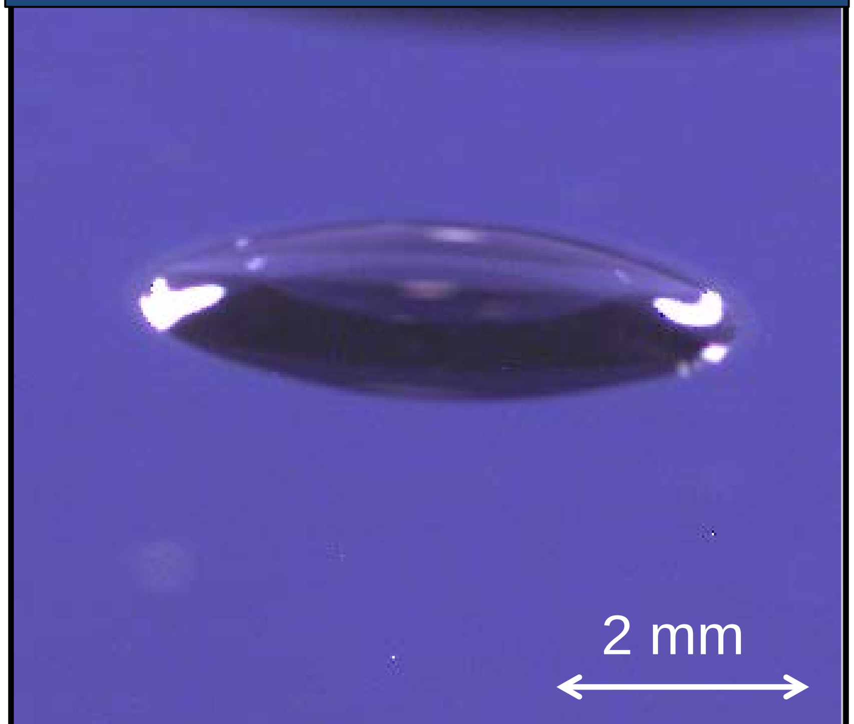
A = peak area

	c
Sol A	14.7%
Sol B	22.7%
Sol C	14.6%
Sol D	5.4%

Sol with lowest ethoxy surface provide greatest TMS coverage

The hydrophobic nature of the HMDS sol can be easily observed using the water droplet test

H_2O drop on standard coating

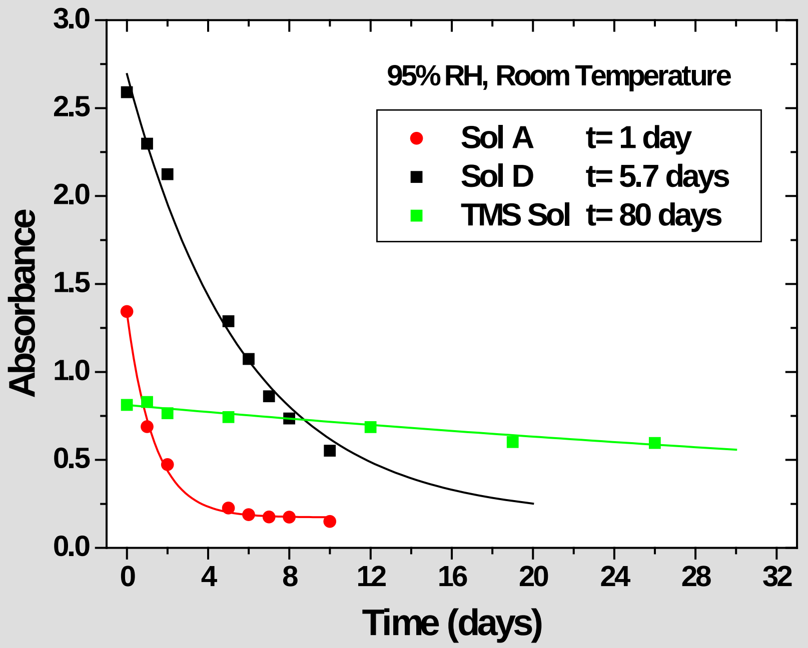


H_2O drop on HMDS coating

Suratwala et. al. *J. Non-Cryst. Solids* 316 (2003) 349

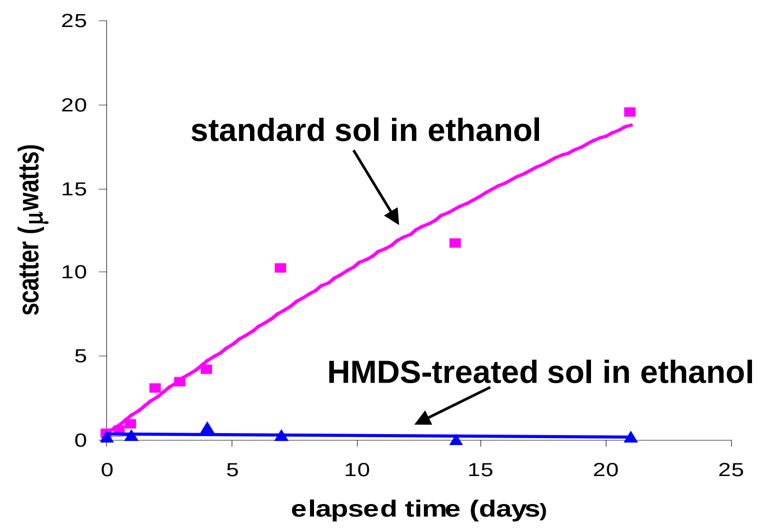
The TMS sol show greater chemical stability and also prevent etchpits on KDP surfaces

Ethoxy IR absorbance (2975 cm^{-1})

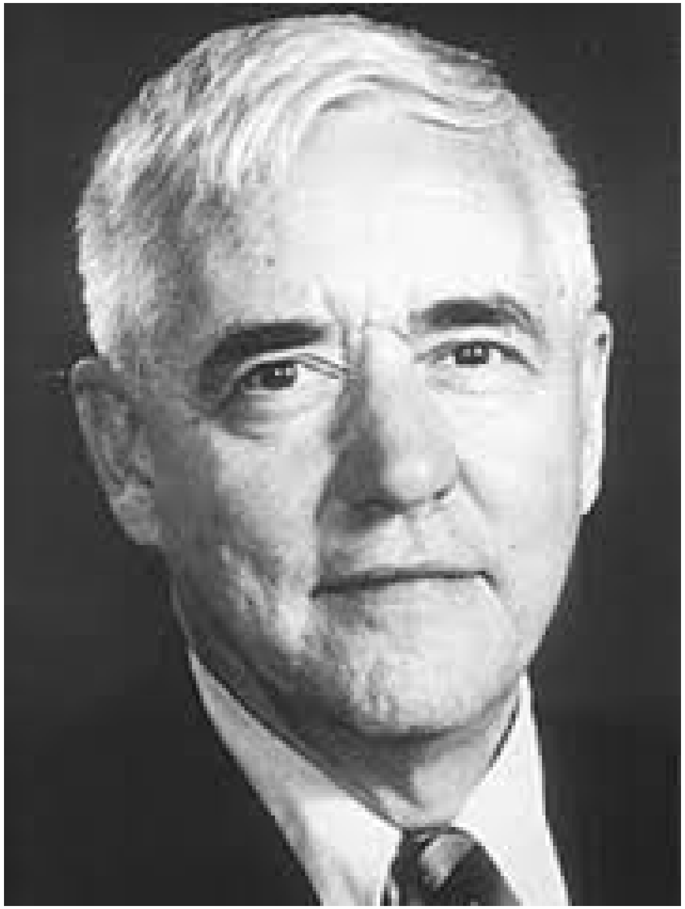


Ethoxy hydrolysis is slowest in TMS sols

Optical scatter vs time



Intermission Story



Dinner at Uhlmann’s house with Eugene

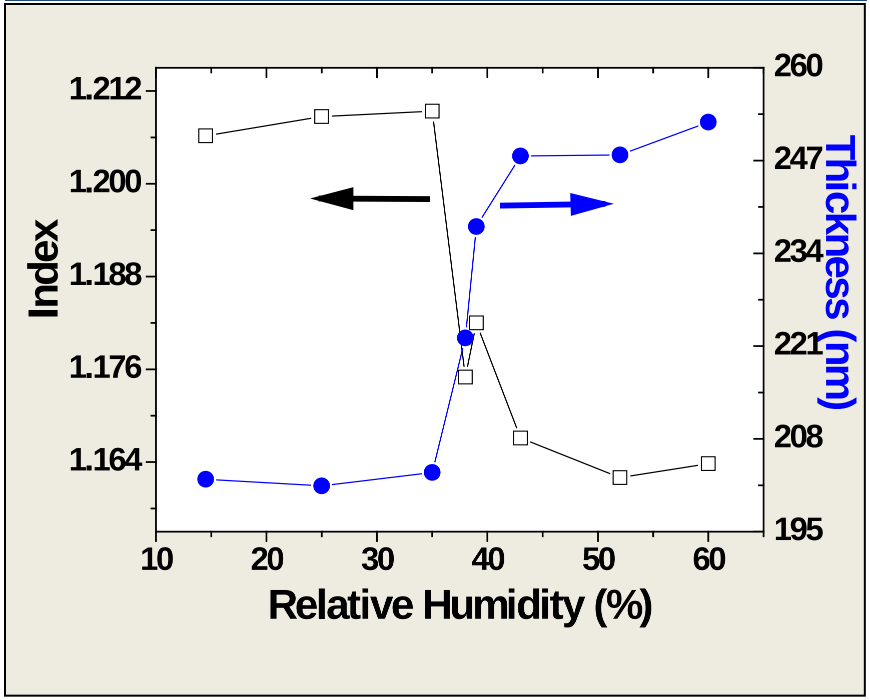
Outline

Surface Chemistry & HMDS Hydrophobic Coating

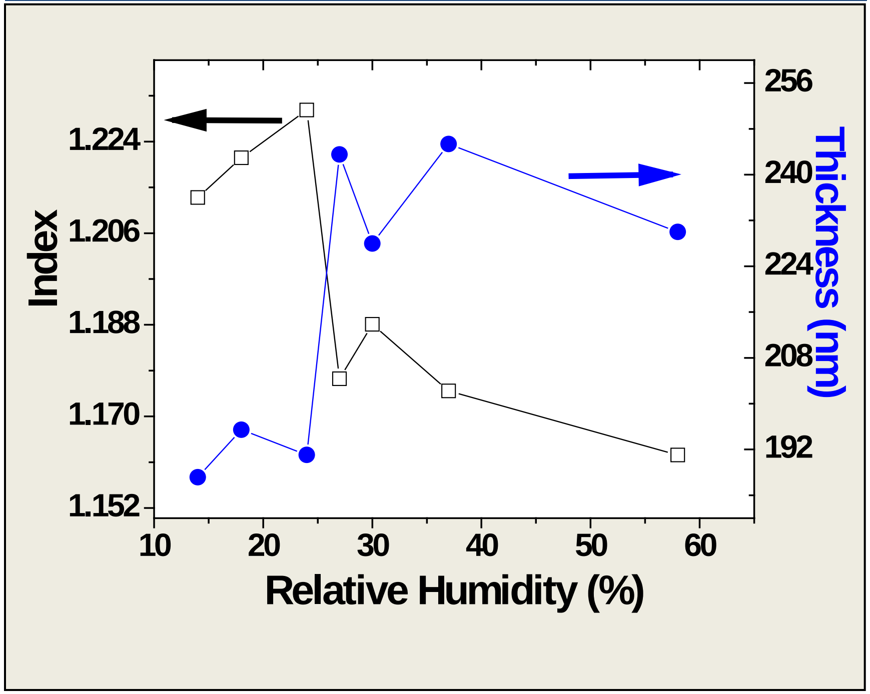
Coating Microstructure (effect of Humidity)

Change in humidity during coating process causes an abrupt change in index and thickness

Sol A : Spin Coating

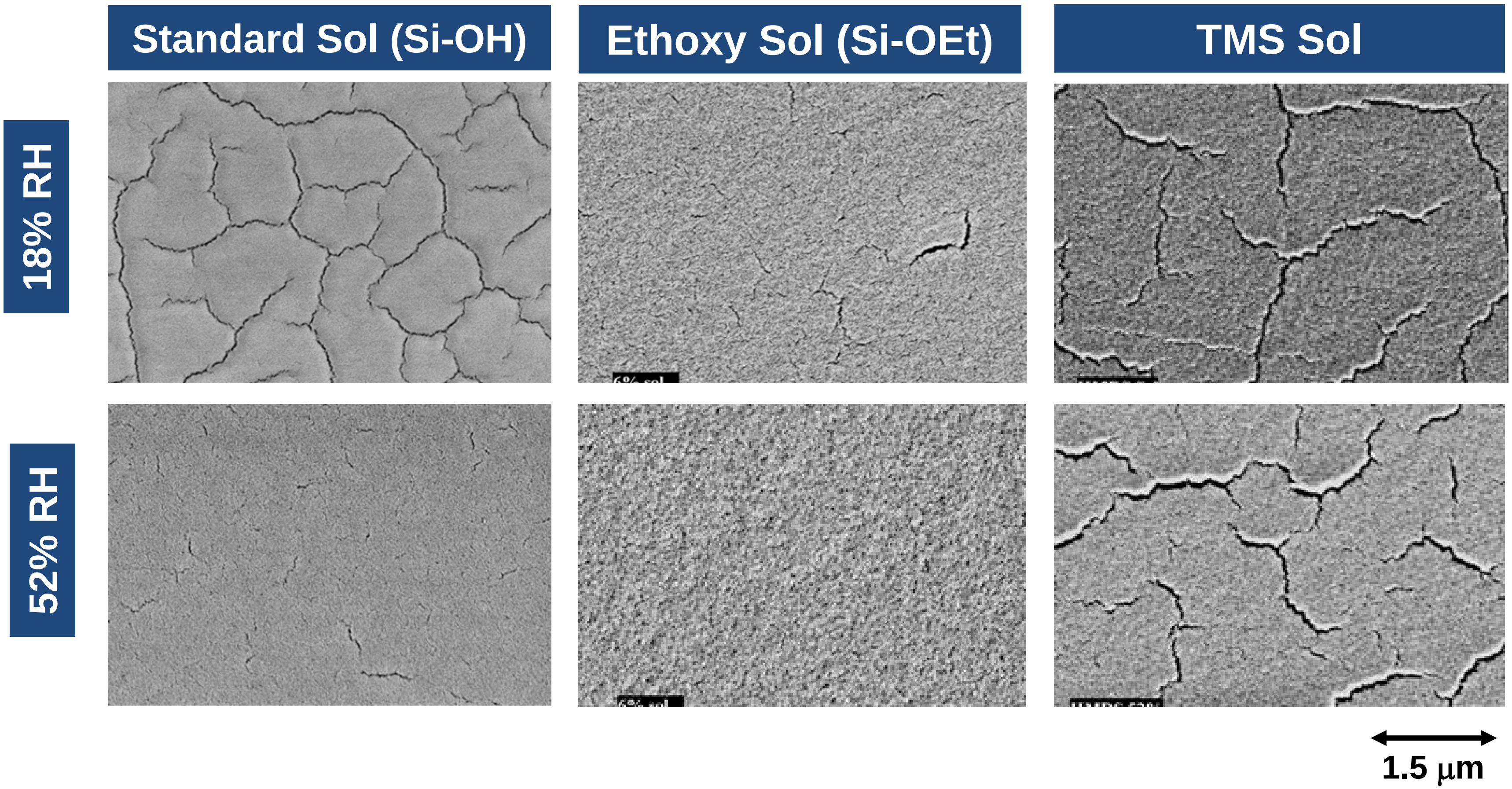


Sol B : Spin Coating



T. Suratwala et. al. *J. Non-Crystal. Solids* 349 (2004) 368

Si-OH sol coating formation is affected strongly by humidity, but TMS sol is not



Shrinkage occurs after the stagnation point because coating mass is constant

Optical Path Length

$$OPL = n_f t_f$$

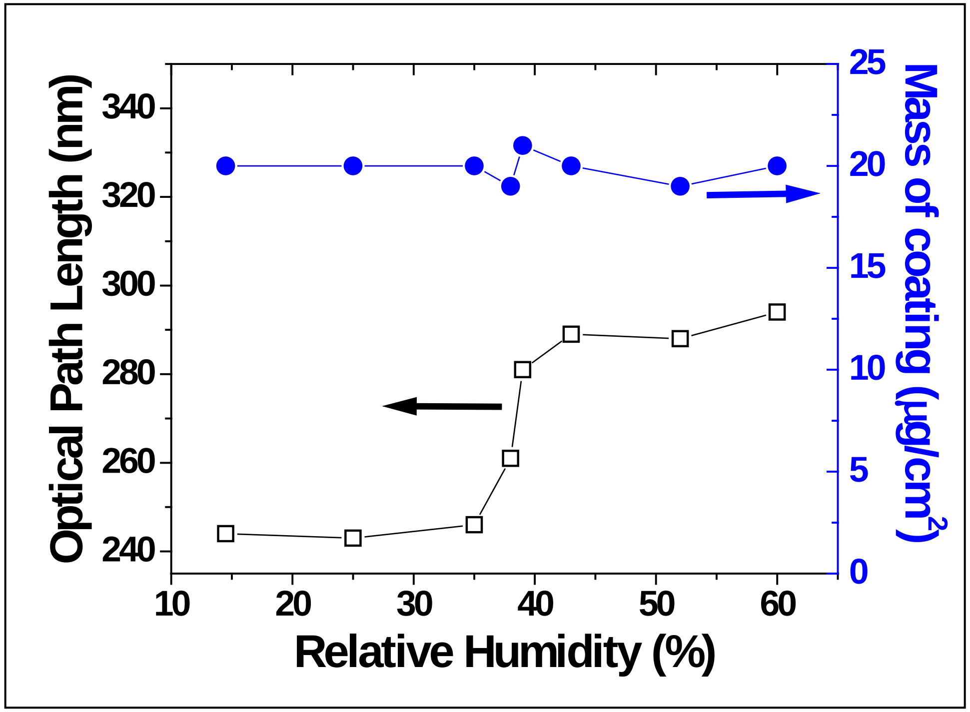
Areal Mass of coating

$$m_f = t_f f_{SiO_2} \rho_{SiO_2}$$

Linear Composite Model

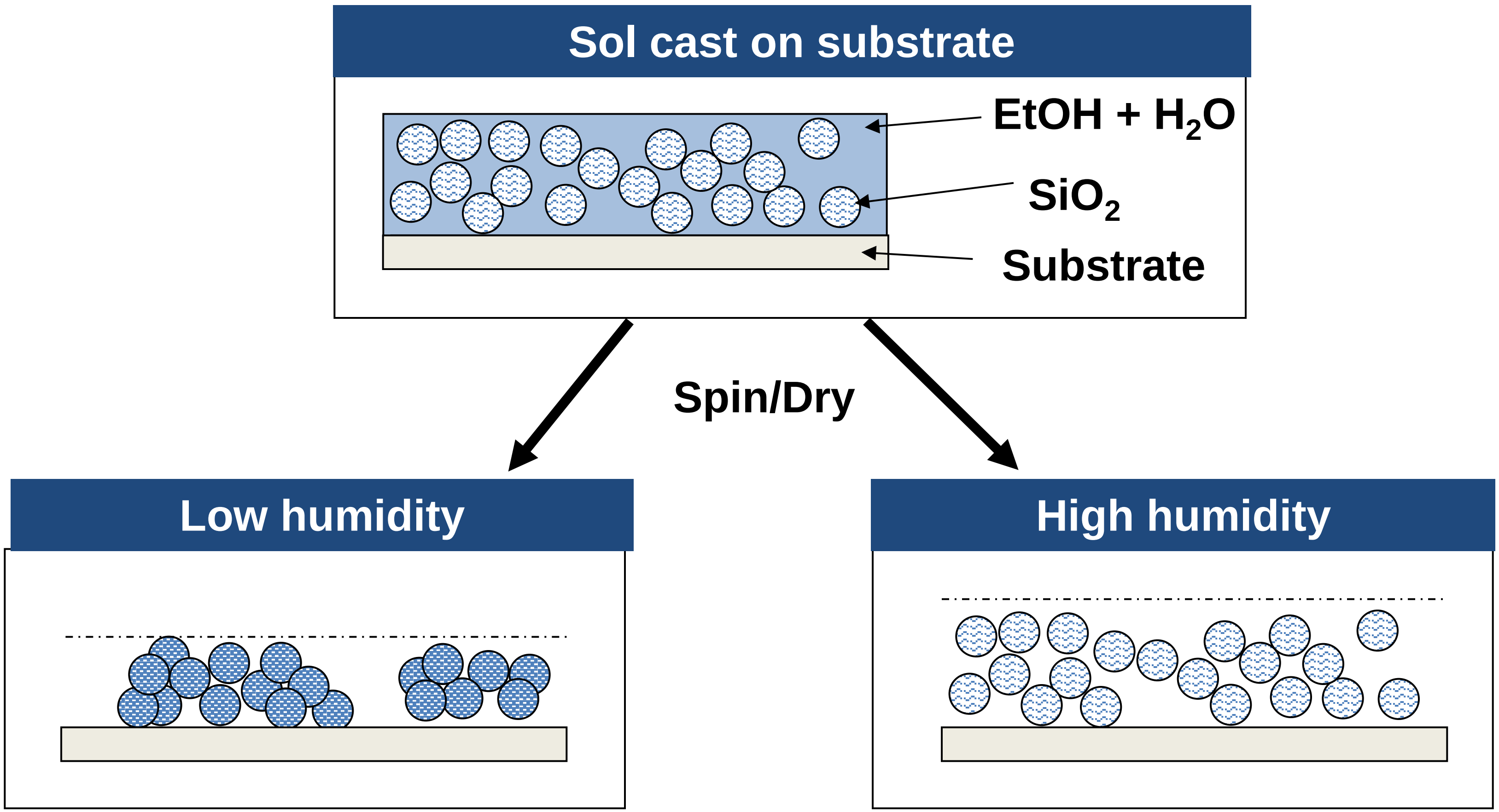
$$n_f = n_{SiO_2} f_{SiO_2} + n_{air} (1 - f_{SiO_2})$$

OPL & Coating mass vs RH



Optical path changes → humidity will affect AR properties
Mass of coating constant → shrinkage due to change in particle packing

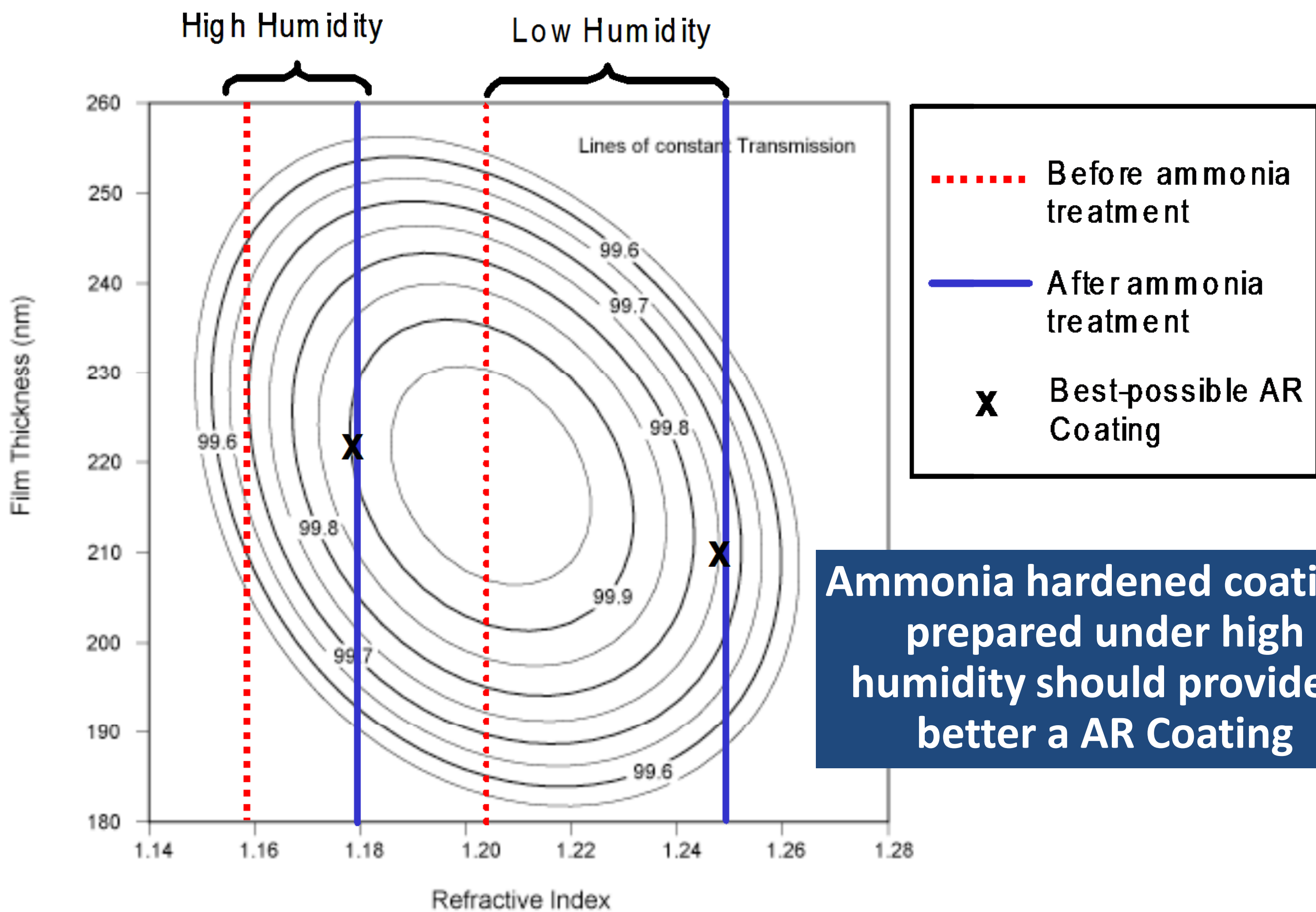
Film shrinkage is governed by balance between pore shrinkage stress (capillary pressure) & silica strength (condensation amount)



- H_2O leave micropores
- Micropores collapse
- Film shrinks & cracks

- H_2O remain in micropores
- Film gains strength
- Film does not shrink

The effect of humidity is accounted for in order to make optimized AR coating



Ammonia hardened coatings prepared under high humidity should provide a better a AR Coating

Acknowledgements

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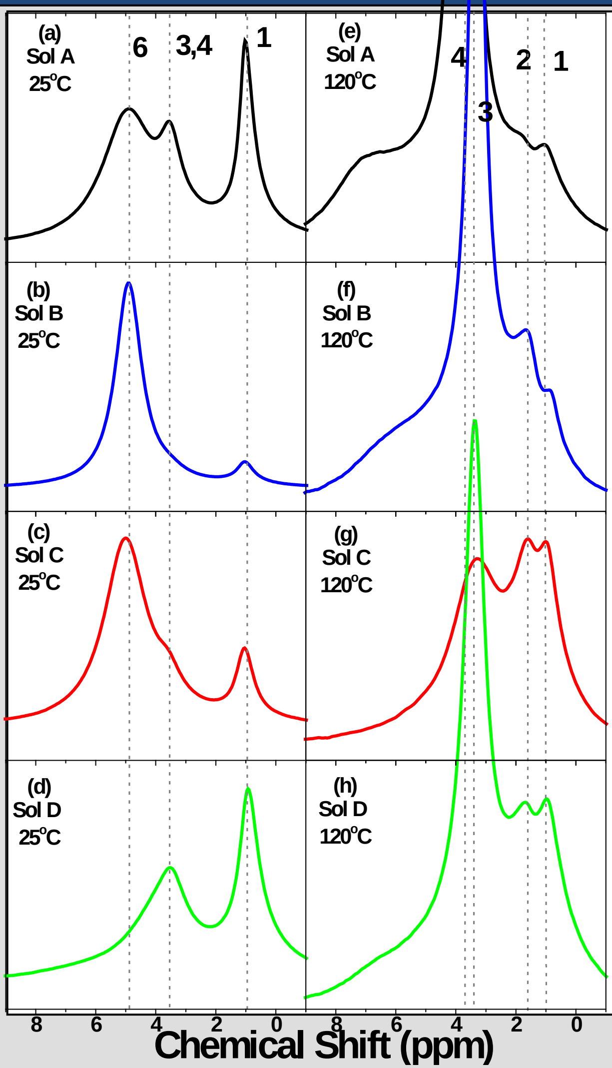
C. Thorsness
D. VanBlarcom
P. Miller

Lawrence Livermore National Laboratory

[1]H MAS NMR is used to quantify surface chemistry of four silica sols

[1]H NMR Spectra



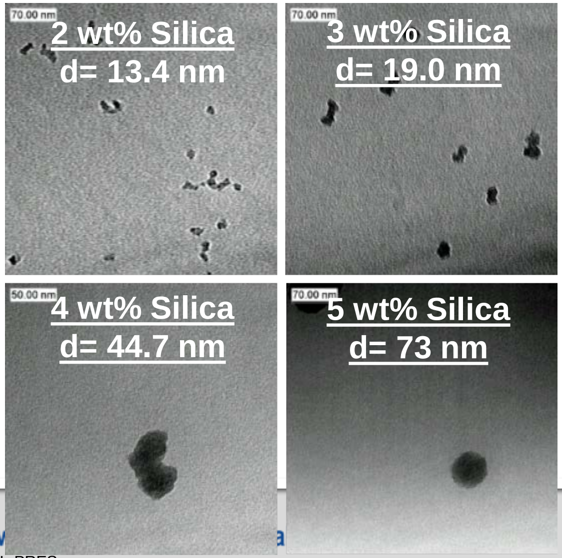
Peak Number	Chemical Shift (ppm)	Chemical species
1	1.0	OCH_2CH_3
2	1.7	Si-OH (isolated)
3	3.5	H_2O (physically absorbed)
4	3.7	OCH_2CH_3
5	1-8 (broad)	Si-OH (hydrogen bonded)
6	4.9	H_2O (Liquid like)

	%OEt	%SiOH (isolated)	%SiOH (Hydrogen bonded)
Sol A	8	17	75
Sol B	2	43	55
Sol C	21	75	4
Sol D	16	43	41

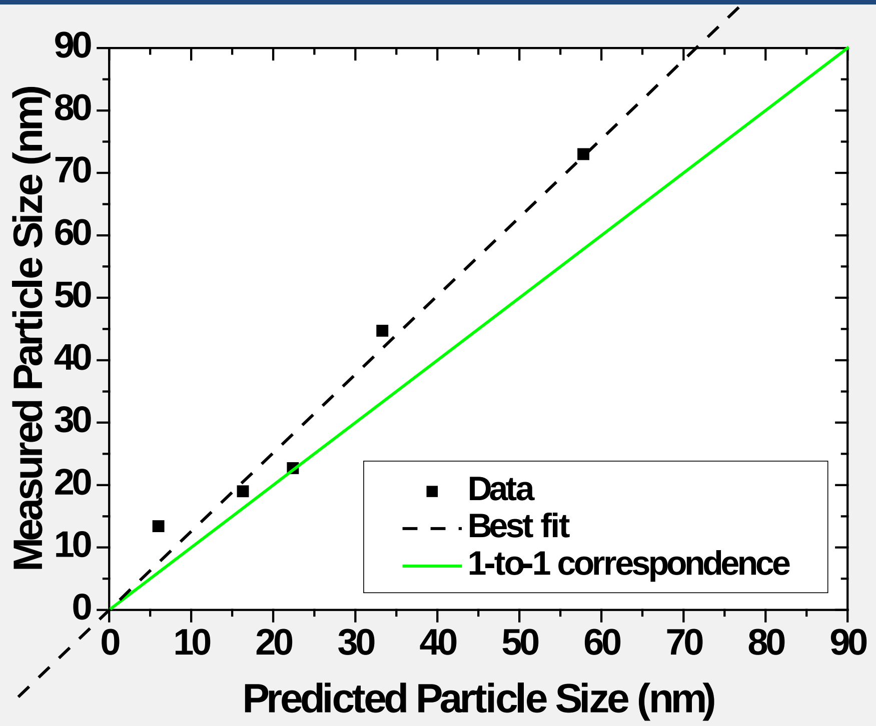
Silica sols can be made to have different ethoxy, isolated silanol, and hydrogen bonded silanols concentrations

There are many factors that effect final particle size of colloids grown by Stober process

Parameter	Effect on Particle Size
[TEOS]	↓
$[NH_3]$	↑
$[H_2O]$	↑
Solvent MW	↑
Temperature	↓



Comparison of measured vs predicted Particle Size



Model by Bogush et. al. Journal of Colloid and Interface Science, 142 (1), (1991)

There are three basic reactions that occur during sol gel processing with various silicate species that can form

Hydrolysis & Condensation

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \longrightarrow \equiv\mathrm{Si{-}OH} + \mathrm{ROH} \quad (1)$$

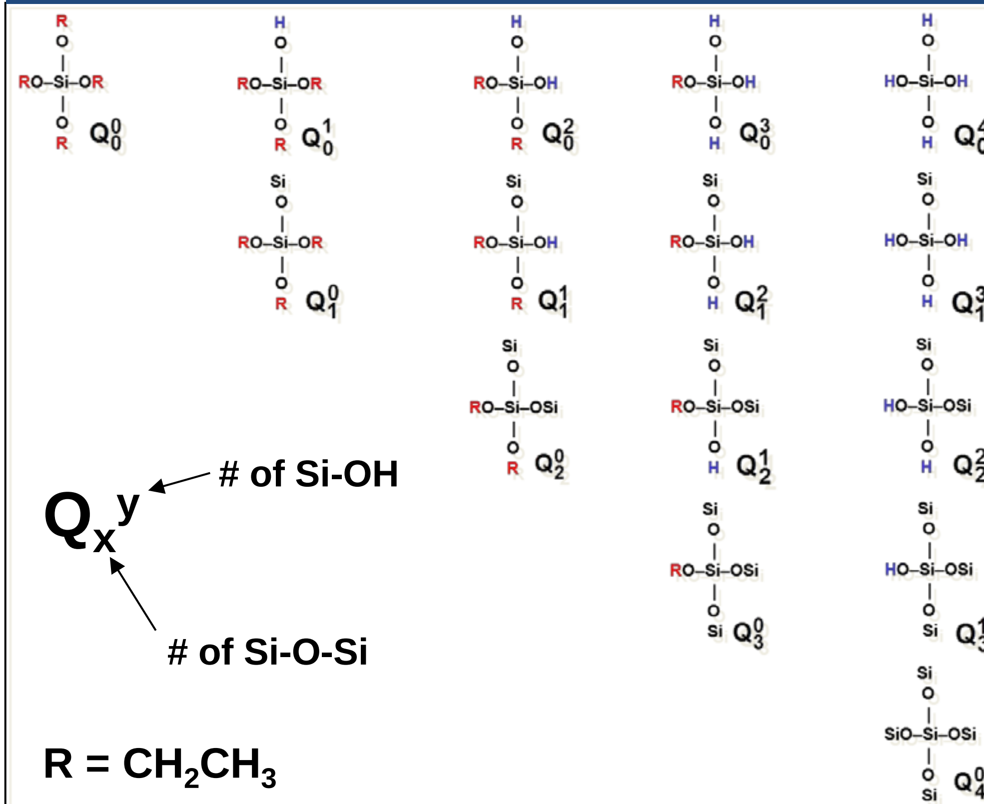
$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}OH} \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \quad (2)$$

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}OR} \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \quad (3)$$

Overall Reaction

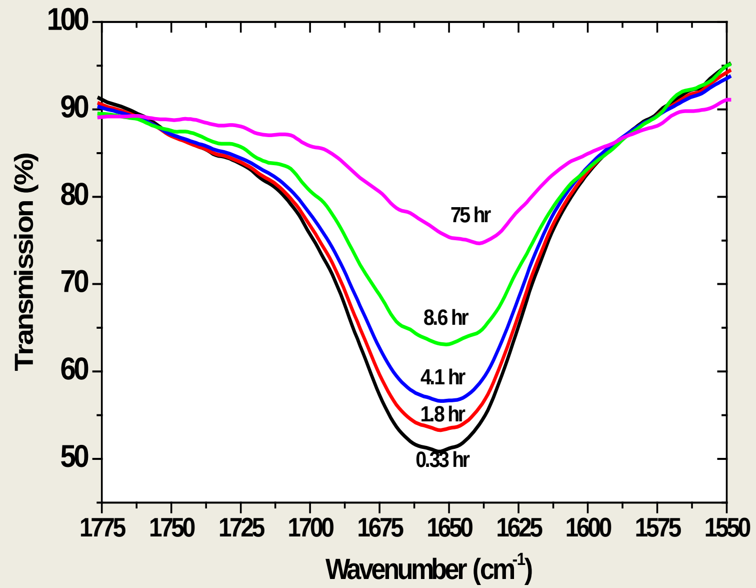
$$\mathrm{Si(OR)_4} + 2\,\mathrm{H_2O} \longrightarrow \mathrm{SiO_2} + 4\,\mathrm{ROH}$$

Various silicate species



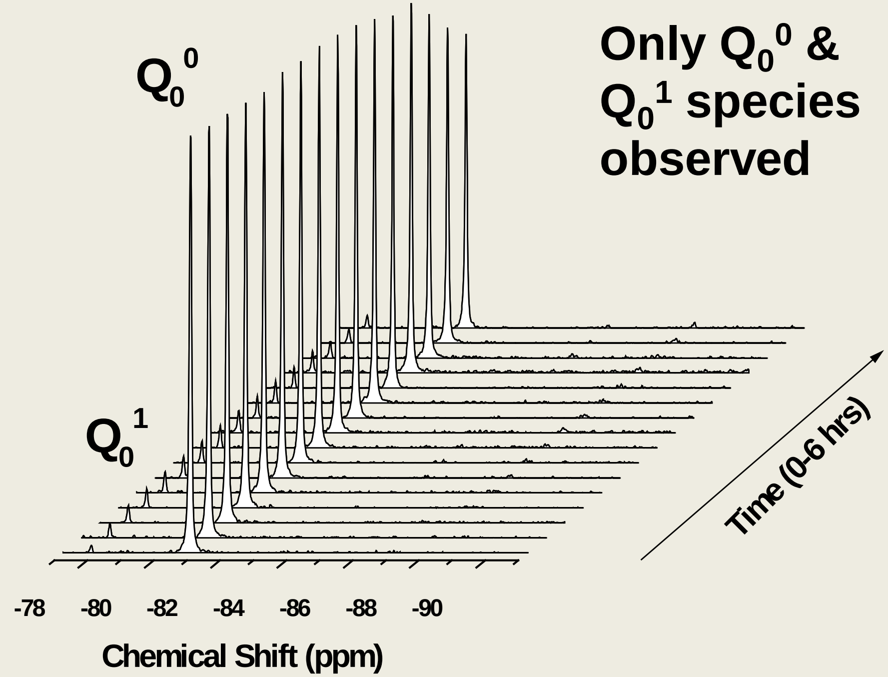
The reaction kinetics were determined by monitoring the H_2O concentration (IR spectroscopy) and selected Q species (solution Si NMR) vs time

IR Spectroscopy



- $[H_2O]$ monitoring the H-O-H bending vibration at 1650 cm^{-1}

^{29}Si Solution NMR



- Q species that become part of the colloid are not detected
- Q_0^0 hydrolysis is rate limiting

Simple kinetic model does a good job at predicting the concentration of species & particle size as a function of time

Rate Equations

$$\frac{d[Q_0^{\,0}]}{dt} = -k_1[Q_0^{\,0}][H_2O]$$

$$\frac{d[Q_0^{\,1}]}{dt} = k_1[Q_0^{\,0}][H_2O] - k_2[Q_0^{\,1}][H_2O]$$

$$\frac{d[H_2O]}{dt} = -k_1[Q_0^{\,0}][H_2O] - k_2[Q_0^{\,1}][H_2O]$$

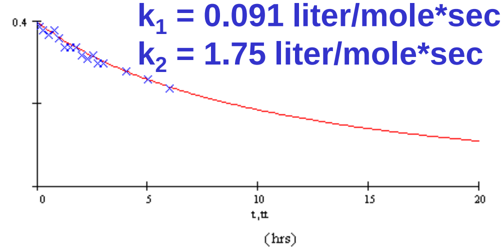
$$\frac{d[Q_0^{\,2}]}{dt} = k_2[Q_0^{\,1}][H_2O]$$

- **The rate of $Q_0^1 \longrightarrow Q_1^0$ is small**
- **Q_0^2 is simply a transient species that quickly condenses to form the colloid**

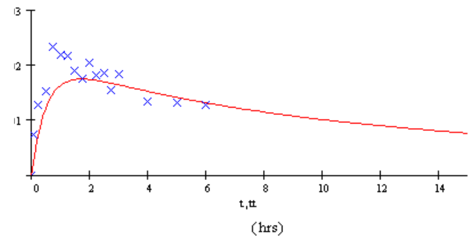
Model Results

k_1 = 0.091 liter/mole*sec
k_2 = 1.75 liter/mole*sec

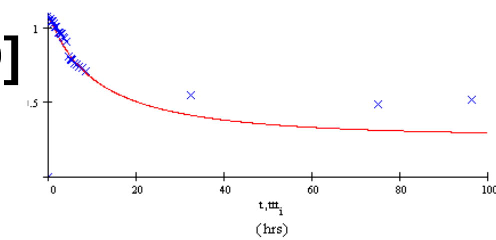
$[Q_0^0]$



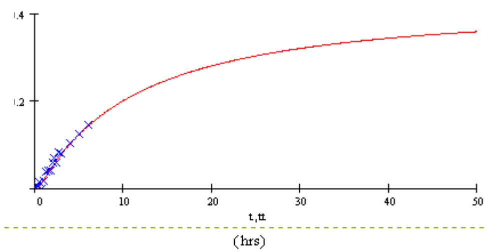
$[Q_0^1]$



$[H_2O]$



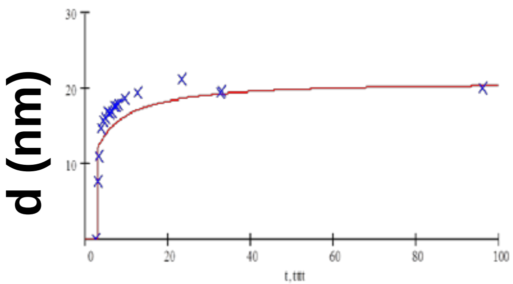
$[Q_0^2]$



Time (hrs)

PS prediction

$$d = \left(\frac{6\,\left[Q_0^2\right]\,MW_{SiO_2}}{\pi\ n\ \rho} \right)^{1/3}$$



Time (hrs)